NASA TECHNICAL TRANSLATION

NASA TT F-13,883

IDENTIFICATION OF PLASTICIZERS IN PLASTICS BY THIN-LAYER CHROMATOGRAPHY

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Translation of "Identyfikacja plastyfikatorow v tworzywach sztucznych za pomoca chromatografii cienkowarstwowej", Polimery, Vol. 14, No. 4, 1969, pp 165-166

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546 OCTOBER 1971

IDENTIFICATION OF PLASTICIZERS IN PLASTICS BY THIN-LAYER CHROMATOGRAPHY

BY

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ABSTRACT: The authors present a method for identifying four sets of plasticizers used in commercial plastics manufacture through chromatography practiced upon a thin layer of an extract of these substances.

One of the most important components of plastics, having great practical /165* significance, consists of the plasticizers. Among the most frequently used plasticizers are ester plasticizers - above 80% (1), which include primarily the phthalates, the sebacates, the adipates, and the phosphates, which are distinguished by the valuable property of not exuding out of plastics.

In the literature a series of studies report experiments on differentiating plasticizers chromatographically (2-6). The results of these investigations enable one to regard thin-layer chromatography of plasticizers as a more advantageously rapid and inexpensive technique than either the filter-paper or the gas technique.

Taking advantage of the experiments of Wandel (3-5) and Braun (6), we investigated a number of solvents and a few absorbents. The best differentiation was achieved on silicon gel G, using a solvent of methylene chloride (in the case of the phosphates) or cyclohexane with the addition of 10% ethyl acetate (for the remaining cases). The method we worked out for the qualitative analysis of ester plasticizers consists of two basic actions securing an ether extract of the material and chromatography of the extracts upon thin layers of silicon gel.

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*Numbers in margin indicate pagination in foreign text.

In order to bring about their differentiation we applied the method of thin-layer chromatography which, along with gas chromatography, is one of the newer analytical techniques. Like all other chromatographic techniques, it serves to differentiate, identify, and quantitatively determine the substances being investigated. It is a type of absorption chromatography; differentiation is determined by the affinity of the investigated substances toward the absorbent used as a stationary phase. It is more advantageous than chemical methods because it is exceptionally sensitive and at the same time simple and quickly performed.

Experimental Part

Equipment and Auxiliary Materials

Glass plates 102 X 133 X 4.5 mm

Glass rod of about 15 mm diameter, having one polished plane surface.

Surgical adhesive tape.

Developing chambers, 120 X 165 X 80 mm.

Glass vaporizer for spraying.

Reagents and Solvents

Silicon gel G (Merck)

Cyclohexane, pure, d.a. [Expansion unknown]

Ethyl acetate, pure, d.a.

Methylene chloride, pure

Developing reagents: iodine vapor, dilute sulphuric acid, solution of potassium bichromate, solution of resorcin in alcohol, solution of antimony chloride in carbon tetrachloride.

Control solutions of plasticizers in alcohol (5-10 percent).

Method of Carrying Out Analysis

Preparation of Ether Extract of Plastic

3-5 grams of well-comminuted plastic are weighed out accurately. This is put into a soxhlet tube, 50 milliliters of ether are added and left overnight. Next, 100 ml of ether are extracted over a boiling water bath for 8-16 hours. The extract is poured into a weighed extraction flask and the

ether is evaporated; the residue is dried and weighed until weight is constant. From the mass of obtained monomer plasticizers a 5-10 percent alcohol solution is prepared; this will be applied to the plates.

Preparation of Plates

1.2 grams of silicon gel G Merck is mixed with 3 ml of water for one minute. The mass secured in this way covers one plate.

The two opposite longer edges of a plate are covered with surgical adhesive tape. Then, the mass of absorbent is poured upon the plate in the form of a paste near one of the uncovered shorter sides. After the mass has been distributed on the plate with the polished rod drawn evenly along the edges covered with tape, a layer of gel material of the thickness of the tape, i.e., about 0.3 mm, is secured. After being dried in air for 20 minutes at room temperature, the prepared plate is then placed in a dryer for 30 minutes, at a temperature of 105°. Next it is transferred to an exsiccator, and there it is preserved above activated silicon gel stained with cobalt salts. To the plate prepared in this way extracts of the substance being examined, plus standard solutions, are applied, and these are chromatographed simultaneously.

Developing the Chromatograph /166

The solutions being investigated are applied to the plates by means of a glass capillary tube, at equal distances (1.5 cm) from each other and from the edges of the plate. Chambers saturated with vapors of a solvent (cyclohexane with 10% ethyl acetate are used for developing. After the leading edge of the solvent has gone 10 cm, the plates are taken out and dried in air for about 20 minutes. They are developed by first inserting them individually into a chamber saturated with iodine vapor. Then, after noting the positions where spots have appeared and after the iodine has been evaporated, they are moistened with appropriate reagents producing color reactions:

1) H_2SO_4 plus water (1 : 1);

2) Solution of potassium bichromate: 5 g. $K_2Cr_2O_4$ dissolved in 15 ml of water, adding 10 ml of concentrated H_2SO_4; moisten with the hot solution;

3) 20% solution of resorcin alcohol, with a small addition of $ZnCl_2$; after moistening with this reagent, heat the plate at 150° C for ten minutes, then after cooling moisten it with 4 n H_2SO_4 and once more heat it for 20 minutes at 120°; moisten the cold plate a third time with a 40% solution in alcohol;

4) Solution of antimony chloride: 5 ml $SbCl_5$ in 10 ml CCl_4; heat the moistened plate to 120° for 10-15 minutes.

Identification of the spots is accomplished through use of the standard samples, developing them side by side on the same plate with the substance being investigated.

In order to illustrate the distribution of the individual spots of plasticizers we set forth below (Table 1) the corresponding R_F values[1].

TABLE I

R_F Values of Plasticizers Developed in 10% Solution of Ethyl Acetate

Plasticizers	R_F
Dimethyl Phthalate	0.22
Dibutyl Phthalate	0.54
Dicyclohexyl Phthalate	0.60
Di-n-Octyl Phthalate	0.79
Di-iso-octyl Phthalate	0.79
Di-2-ethylhexyl Phthalate	0.79
Dinonyl Phthalate	0.78
Didecyl Phthalate	0.79
Di-iso-decyl Phthalate	0.86
Dimethyl Sebacate	0.41
Di-ethyl Sebacate	0.53
Di-octyl Sebacate	0.67

[1] R_F is the ratio between the distance of the center of the spot and the distance of the leading edge of the mobile phase from the start.

Table I continued:

Di-2-ethylhexyl Sebacate	0.81
Di-ethyl Adipate	0.39
Dibutyl Adipate	0.56
Dicyclohexyl Adipate	0.63
Dioctyl Adipate	0.71
Tricresyl Phosphate	0.36
Triphenyl Phosphate	0.04
Phenyl-dicresyl Phosphate	0.18
Trioctyl Phosphate	0.36

Figure 1 illustrates the distribution of color spots of plasticizers.

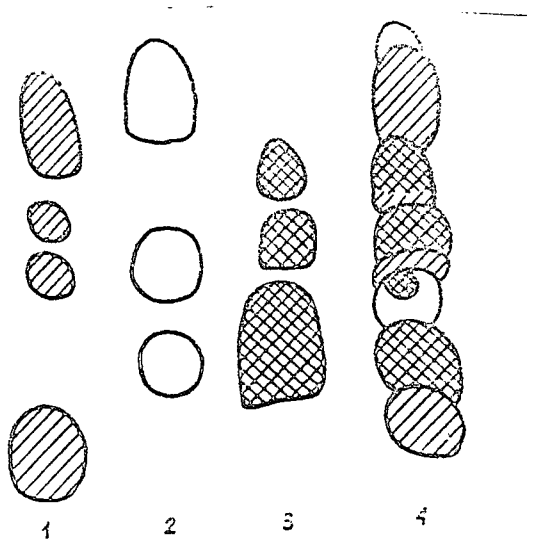

Figure 1. Thin-layer Chromatogram of Plasticizer: 1. Phthalates; 2. Sebacates; 3. Adipates; 4. Spots of Individual Plasticizers Superimposed Upon one Another.

Discussion of Results

As a result of the investigations the conditions for optimum differentiation of phthalates, sebacates, adipates and phosphates have been determined. Considering the physical impossibility (distance of leading edge from start amounts to 10 cm) of achieving differentiation of all esters, particular attention is devoted to the working out of an identification such that on the basis of distinguishing between the colors of the spots of the chromatogram it will be possible to draw conclusions regarding the plasticizers present on it.

The most suitable developing agent proved to be resorcin, which brought about the appearance of phthalate (orange), adipate (cherry-red), and sebacate (yellowish white) color spots. This made it possible to distinguish plasticizers and classify them in groups. The defective potential of the method is about 10 μg of plasticizer.

The phosphates do not stain under the influence of the resorcin reagent and remain invisible even after development. But they can easily be identified by moistening the plate with a solution of antimony chloride in carbon tetrachloride. Dark spots immediately appear. Detective potential of the method: 2-3 μg of phosphates.

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Translated for the National Aeronautics and Space Administration under contract No. NASw-2037 by Techtran Corporation, P. O. Box 729, Glen Burnie, Maryland, 21061, translator: H. B. Wells.